



Vanadium pyrophosphate oxides: The role of preparation chemistry in determining renewable acrolein production from glycerol dehydration

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ABSTRACT

Efficient acrolein production through selective dehydration of biomass-derivable glycerol was investigated over the vanadium pyrophosphate oxide (VPO) catalysts. Employing polyethylene glycol (PEG) additive in the preparation media and activating the VPO precursors in the butane–air atmosphere considerably enhanced catalyst performance for the target reaction. An acrolein yield of 70.1 mol% can be achieved over the as-synthesized VPO catalyst using an aqueous glycerol solution (36.5 wt%) feed and a liquid hourly space velocity (LHSV) of 4 h⁻¹ at 320 °C. Moreover, the derived VPO catalyst can handle heavy loading of reaction feed, such as a concentrated glycerol solution (50.0 wt%) or a notably high LHSV of 12 h⁻¹, and still retain reasonable acrolein yields (45–65 mol%), giving acrolein formation rate up to 35.3 mmol g_{cat}⁻¹ h⁻¹. Techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and hydrogen temperature programmed reduction (H₂-TPR) were employed to explore the nature of catalysts. Type of alcohol and addition of PEG adopted in catalyst preparation showed significant impact on sample crystallinity/morphology, surface V⁵⁺/V⁴⁺ ratio, V–O bonding strength, and Brønsted surface acidity. Balanced surface V⁵⁺/V⁴⁺ ratio and suitable density of medium strong acid sites are found to be critical to accomplish superior activity.

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1. Introduction

As fossil resources deplete and increasing concerns about environmental issues, the utilization of biomass-derivable feedstock is of great interest [1–3]. The biomass-derivable glycerol has gained considerable attention because of its continuous availability in huge amount from the biodiesel production process and its capability of being a prominent chemical to synthesize value-added products. Considerable efforts have been devoted to the transformation of glycerol by various catalytic processes involving oxidation, (oxi)dehydration, reforming, etherification, esterification, hydrogenolysis, and so on [4–14].

The most significant direct application of acrolein is as an herbicide to control the growth of aquatic plants. Acrolein is also an important bulk chemical used as feedstock for production of acrylic acid, pharmaceuticals, fiber treatments, etc. The current method for manufacturing acrolein is based on oxidation of propylene or

propane derived from petroleum, therefore, carbon-neutral processes for producing acrolein from glycerol will lead to lower oil consumption and reduced environmental impact.

Catalytic dehydration of glycerol to acrolein has attracted great interest. Lauriol-Garbey et al. [12] studied acid–base properties of niobium–zirconium mixed oxide catalysts for glycerol dehydration by calorimetric and catalytic measurements. Cavani et al. [13] investigated the control of selectivity in gas-phase glycerol dehydration to acrolein catalyzed by sulfated zirconia. Recently Katryniok et al. [15] overviewed the developments in the catalytic dehydration of glycerol to acrolein over the zeolite-type, heteropoly acid-type, and mixed oxide-type catalysts with respect to the observed catalytic performance as well as catalyst durability. Dubios et al. [16] reported a process for producing acrolein by gas-phase dehydration of glycerol in the presence of strongly acidic solid catalysts with Hammett acidity (H₀) between –10 and –16. Tsukuda et al. [17] investigated the production of acrolein from glycerol over silica-supported heteropoly acids. It was found that silicotungstic acid supported on mesoporous silica showed the highest activity: acrolein selectivity of 85 mol% at 548 K. They also supposed a possible reaction route. Recently, acrolein synthesis

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from glycerol in hot-compressed water was studied by Watanabe et al. [18]. Glycerol conversion was conducted in pressurized hot water (573–673 K, 25–34.5 MPa) using both batch and flowing apparatus. Approximately acrolein selectivity of 80% was obtained at glycerol conversion of 90%. Chai et al. [19] used ZrO₂- and SiO₂-supported 12-tungstophosphoric acid catalysts and acrolein yield of 54% was obtained over the HPW/ZrO₂ catalysts. Chai et al. [20] also applied amorphous Nb₂O₅ catalyst having the highest fraction of acid sites with Hammett acidity being $8.2 \leq H_0 \leq 3.0$ for the reaction, and achieved notably high mass specific activity. Later on Xu and his co-workers extended selective glycerol dehydration over tantalum oxide and other systems [21–23]. Liu et al. [24] recently reported glycerol dehydration over the rare earth pyrophosphates and found that the pyrophosphate catalysts were active and selective toward acrolein production. They reported that catalytic activities were greatly influenced by the doped rare earth elements, and the Nd₄(P₂O₇)₃ catalyst exhibited 80% selectivity to acrolein at glycerol conversion of 87%. Moreover, many zeolites and modified-zeolites were tested in glycerol dehydration [25–28].

The most well-known pyrophosphate catalysts should be the vanadium pyrophosphate oxides (VPO). The VPO type catalysts have been extensively studied in the selective oxidation of butane, isobutene, propane, and ethane to the corresponding acids [29–34]. This kind of catalyst was recognized as one of the most complicated catalyst systems, and many efforts have been made to advance our understanding of catalyst nature in the partial oxidation of *n*-butane to maleic anhydride [35–43,32,44–47].

The VPO catalysts can be obtained via the dehydration of the important precursor, namely, vanadyl phosphate hemihydrate (VOHPO₄·0.5H₂O). Ueda's group first studied glycerol dehydration over both a VPO precursor and an activated VPO catalyst, and found that both of them were active for the reaction [48,49]. Interestingly, the VOHPO₄·0.5H₂O precursor outperformed the activated vanadium pyrophosphate oxide catalyst, and the former also performed with maximized carbon balance (i.e., very low carbon deposition rate in reaction). It is known that preparation history (the kind of alcohol in preparation medium and the catalyst activation in particular) can have an intensive impact on the properties of VPO catalyst, including phase composition, morphology, particle size, and surface P/V ratio. It is also generally accepted that the structure of active phase and the role of V⁵⁺ species are the key factors for catalytic oxidations over the VPO-type catalysts [50–52]. Very recently, we found that the carefully tuned VPO catalyst comprising dominated δ-VOPO₄ and (VO)₂P₂O₇ components through an activation under an atmosphere with very low butane concentration (0.3 vol.% butane in air) was highly efficient for the aldol condensation between methyl acetate and formaldehyde to acrylic acid and its derivative [53]. In this study, we synthesized the VPO catalysts by employing different alcohols as reducing agents and solvents and the polyethylene glycol (PEG) as a specific additive in preparation medium, for glycerol dehydration to acrolein. Our previous studies confirmed that the PEG-addition in catalyst preparation can dramatically affect the physicochemical properties of VPO-type catalyst for butane selective oxidation; while the current study clearly demonstrated the role of preparation chemistry in determining the catalytic behavior of selective dehydration of glycerol to acrolein on this type of catalyst. The obtained results are informative for understanding the target reaction on the carefully identified components of VPO catalyst.

2. Experimental

2.1. Catalyst preparation

The catalyst precursors were synthesized as described previously [54]. Mixed iso-butyl and benzyl alcohols (volume ratio of

1:1) were adopted as the preparation medium. V₂O₅ was first refluxed at 140 °C for 6 h, after that PEG 6000 was introduced in suitable amount. One hour later, phosphoric acid (85%) was added drop wise to reach a P/V atomic ratio of 1.05/1.0. After another 6 h of refluxing, the suspension was filtered and the solid was washed with iso-butanol and acetone, and then dried at 100 °C in air for 24 h. The obtained precursor was denoted as PVPO_{PEG-a}.

Single benzyl alcohol was also used as the preparation medium. The other preparation steps are the same described above for PVPO_{PEG-a} preparation. The as-synthesized precursor was denoted as PVPO_{PEG-b}.

Besides the precursors prepared by employing PEG additive, the reference precursor was also synthesized without using PEG, and the synthesis procedures were essentially the same except for PEG6000 introduction. The obtained precursor was denoted as VPO_{NPEG}.

Before characterization and performance evaluation, all of the precursors were activated according to the following procedure. A dried precursor of 5 g was heated up from room temperature (RT) to 400 °C at a rate of 2 °C/min in a mixture of *n*-butane, N₂, and O₂ (1.5/17.2/81.3, v/v/v) with a flow rate = 20 ml min⁻¹ and kept at this temperature for 15 h. The samples after activation were denoted as VPO_{PEG-a}, VPO_{PEG-b}, and VPO_{NPEG}, respectively.

2.2. Catalyst evaluation

The evaluation of catalyst activity was carried out in an upright fixed-bed quartz reactor that was 8 mm in inner diameter and 500 mm in length. The reaction was operated at atmospheric pressure. Catalyst of 0.5 g was charged into the reactor, and the space above the catalyst bed was filled with quartz chips to ensure preheating of the in-coming liquid. Before introduction of the feedstock, the sample was heated up in a flow of pure N₂ (18 ml min⁻¹) to a desired temperature at a rate of 10 °C/min and kept at this temperature for 80 min. The reaction temperature was monitored by a thermocouple inserted into the catalyst bed. After that, carrier gas was changed to a N₂–O₂ mixture (92/8, v/v). Aqueous glycerol solution (36.5 wt%) was fed at a LHSV of 4 h⁻¹ by a syringe pump, and the products were collected in a cold trap after 2-h reaction. The analysis of the collected liquid was conducted using a gas chromatograph equipped with flame ionized detector (FID) and HP-FFAP capillary column (0.32 mm × 25 m), and isobutanol was adopted as an internal standard.

Glycerol conversion (%) was defined as the moles of glycerol reacted divided by the moles of glycerol fed while the product selectivity (mol%) was defined as the moles of carbon atoms in a defined product divided by the moles of carbon atoms in the reacted glycerol.

2.3. Characterization

Scanning electron microscopic (SEM) images of samples were taken on an S-4800 SEM instrument. X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert MPD Pro X-ray diffractometer with graphite-monochromatized Cu K_α radiation (λ = 0.1541 nm). Raman spectra were recorded at RT on a LABRAM-HR Raman spectrometer (laser source: 514.3 nm; power: 1.0–1.5 mW). H₂-TPR was performed from RT to 800 °C at a rate of 10 °C/min in a flow of H₂/N₂ mixture (5/95, v/v) with a flow rate = 40 ml min⁻¹, and isothermally held at 800 °C until reduction was complete. TG/DTA measurement was conducted on a NETZSCH STA-449C integrated thermo-analysis instrument with the sample heated in air at a rate of 10 °C/min from RT to 700 °C. Ammonia temperature-programmed desorption (NH₃-TPD) was carried out to measure surface acidity of catalysts. Typically, 0.05 g of catalyst was heated in flowing He (30 ml min⁻¹) at 400 °C for 1 h, and

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